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	COLORED MAGNETIC TONERS, PROCESSES FOR THEIR PREPARATION AND THEIR USE.				

5 Colored Magnetic Toners, Process for their preparation and
their use

10 BACKGROUND OF THE INVENTION

The present invention relates to colored magnetic
toners containing binder, coloring agent and magnetizable
material, processes for their preparation, and the use of
these toners.

15 Toners are the coloring components of modern widely
used electrostatic photocopying systems. Black toners are
normally used. Black magnetic toners contain iron powder,
chromium dioxide, gamma-iron oxide, magnetite or ferrite
powder as magnetizable substance.

20 Also, attempts have been made to use colored toners
in order to be able to produce colored photocopies. In the
case of magnetic one-component toners for photocopying
processes or magnetic printers, the strong natural color
normally present in the magnetizable component of the
25 toners is found to be an impediment to the production of
colored toners in a pure color.

In European Patent 75 346 (=US 4.443.527) a compli-
cated process of masking the natural color of a magne-
tizable core by covering it with the coloring component
30 has been proposed to overcome this disadvantage.

Another proposal for the preparation of red or brown
toners is the use of gamma-iron oxide containing
alpha-iron oxide according to German Patent 3 313 788
(=US 4.448.870). It is a disadvantage of this process that
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5 such gamma-iron oxide magnetically diluted with non-magnetic alpha-iron oxide has a lower magnetic saturation than pure gamma-iron oxide. A larger quantity is therefore required compared with pure gamma-iron oxide for achieving a certain magnetic quality of the toner.

10 In German Patent 3 315 005, moreover, it is proposed to use magnetic particles, preferably produced by sintering, having an average diameter of from 0.5 to 3.5 μm . A disadvantage of this proposal is that a relatively wide particle size distribution is obtained so that a proportion
15 of small pigment particles with intense color is also present.

It is therefore an object of the present invention to provide a colored magnetic toner which enables photocopies of magnetic prints to be produced in highly
20 saturated color.

BRIEF DESCRIPTION OF THE INVENTION

It has now surprisingly been found that when
25 platelet-shaped or scale-like magnetizable particles are used as magnetic component of a one-component toner, the color of the toner is determined only to an insignificant extent by the natural color of the magnetic component and mainly by the intensely colored coloring agent added.

30 The present invention therefore relates to colored magnetic toners comprising binder, coloring agent and magnetizable material wherein the magnetizable material is in the form of platelet-shaped or scale-like magnetic particles.

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DETAILED DESCRIPTION

10 The platelet-shaped magnetizable particles used may in particular be such particles of iron or ferrite (e.g. barium ferrite). Iron oxides having the composition FeO_x wherein $1.33 \leq x < 1.5$ are particularly preferred as platelet-shaped magnetic particles. Platelet-shaped alpha-iron oxide is suitable as a starting component for the preparation of such an iron oxide. This is available in the form of natural Waldenstein mica (micaceous iron
15 oxide). Substantially better results, however, are obtainable when synthetic platelet-shaped alpha-iron oxide (as described e.g. in German Patent 3 019 404 (= US 4.289.746) and in European Patent 14 382) (= US 4.404.254) is used.

20 The platelet-shaped alpha-iron oxide can be converted into magnetite by reducing with reducing agents (preferably with hydrogen at 250 to 600°C) without loss of form. The magnetic pigment obtained may be used directly as magnetic component in the toners according to the invention.

25 The diameter of the magnetic particles used in the toner according to the invention lies above the optimum particle size for color pigments, and is preferably from 0.5 to 25 μm , and the diameter/thickness ratio is preferably ≥ 5 . It is advantageous to use magnetic particles containing as few as possible small particles and having
30 a narrow particle size distribution.

Furthermore, these particles should undergo little or no sintering during their preparation as sintering could have a deleterious effect on their dispersibility. They can then be readily converted into a good state of
35 dispersion in a binder or binder solution, simply by stirring, without the expenditure of special dispersing energy.

5 The binders suitable for the present invention are those binders customarily used in toner compositions and which are well known to those skilled in the art preferred in the toner according to the present invention are of the kind containing polymers or copolymers based on polystyrene, polyesters, polymethacrylate or polyethylene, as indicated inter alia in German Patent 3 315 005.

Typical binders are the following:

Resins of the styrene type (homopolymers or copolymers which contain styrene or substituted styrene), e.g.
15 polystyrene, polychlorostyrene, polymethylstyrene, styrene/chlorostyrene copolymer, styrene/propylene copolymer, styrene/butadiene copolymer, styrene/vinyl chloride copolymer, styrene/vinyl acetate copolymer, styrene/maleic acid copolymer, styrene/acrylic acid ester
20 copolymer (styrene/methyl acrylate copolymer, styrene/ethyl acrylate copolymer, styrene/butyl acrylate copolymer, styrene/octyl acrylate copolymer, styrene/phenyl acrylate copolymer, etc.) Styrene/methacrylic acid ester copolymer (styrene/methyl methacrylate copolymer,
25 styrene/ethyl methacrylate copolymer, styrene/butyl methacrylate copolymer, styrene/phenyl methacrylate copolymer, etc.), ethylene/methyl chloracrylate copolymer and styrene/acrylonitrile/acrylic acid ester copolymer, polyvinyl chloride, ethylene/vinyl acetate copolymer,
30 resin-modified maleic acid resin, phenolic resin, epoxide resin, polyester resin, low-molecular polyethylene, low-molecular polypropylene, monomer resin, polyurethane resin, silicone resin, ketone resin, ethylene/ethyl acrylate copolymer, xylene resin and polyvinyl butyrate
35 resin can be used. The above-mentioned resins can be used singly or in combination with one another.

5 Numerous materials are suitable for colouring agents in the present invention. Particularly suitable are the customarily used coloring agents including the organic and/or inorganic coloring agents such as those described inter alia in German Patent 3 315 005 and European Patent 75 346
10 (= US 4.443.527).

Typical coloring agents are:

A. Red coloring pigments

Insoluble azo pigments such as toluidine red (PR3, CI 12120), para red (PR 1, CI 12070) and chlorinated para
15 red (PR4, CI 12085).

Naphthol red pigments, such as pigment red 2 (CI 12310), pigment red 5 (CI 12490), pigment red 14 (CI 12380), pigment red 17 (CI 12390), pigment red 18 (CI 12350), pigment red 22 (CI 12315), pigment red 23
20 (CI 12355), pigment red 31 (CI 13360) and pigment red 112 (CI 12370). Lithol red pigments such as sodium lithol red (PR 49), barium lithol red (PR 49 : 1), calcium lithol red (PR 49 : 2).

Anionic azo dyes, such as the rubines: lithol rubine
25 PR 57 (CI 15850) and calcium red (PR 52, CI 15860), manganese red (PR 52, CI 15860), the group Permanent Red 2B, such as barium red 28 (PR 48 : 1, CI 15865), calcium red 2B (PR 48 : 1, CI 15865) and manganese red 2B (PR 48 : 4, CI 15865).

30 Polycyclic pigments, such as Alizarine lake (PR 83, CI 58000 : 1), Thio-indigo pigments (PR 86, 87, 88, 181, 198), VAT-pigments such as the perylene pigments (e.g. PR 123, 149, 179, 190), and the non-perylene-pigments (e.g. PR 177), and Chinacridon pigments (PR 122, 192, 209). In-
35 organic pigments, such as cadmium selenide, iron oxide, and various chromates.

5 B. Blue coloring pigments

Copper phthalocyanine (PB 15, CI 74160), Iron blue (PB 27, CI 77510), Ultramarine blue (PB 29, CI 77007), Cobalt blue (PB 28, CI 77346) and Dianasidine blue (PB 25, CI 21180). Basic dye pigments (basic dyes which have reacted with complex or heteropoly acids, such as phospho-

10 tungstic acid and phosphomolybdic acid), alkali blue pigments (PB 18, 19), and VAT-pigments (PB 21, 22, 60, 64).

C. Green coloring pigments

Halogenated copper phthalocyanine (PG 7, 37),

15 chromium green and Pigment green B (PB 8).

D. Yellow coloring pigments

Hansa yellow (CI 1168), Benzidine yellow (CI 21090), Azo-pigments (CI 13096), Anthrapyrimidine (CI 6842), Nickel titanium yellow (CI 77788). Chromate pigments

20 (CI 77603) and Iron oxide yellow (CI 77492).

The inorganic pigments, which are frequently less attractive in terms of toxicology and/or ecology, although they are opaque, may be replaced, for example, by a series of Solintor pigments made by Messrs. Intorsa, of Barce-

25 lona, such as Solintor Red RN (PR 3), Solintor Lake Red LC-O (PR 53) and Solintor Scarlet RN. Equally well usable is a series of azo-pigments made by Messrs. Hoechst, e.g. Permanent Red F3 RK 70 (PR 170), Permanent orange RL 70 VP (PO 34), Permanent orange HL 70 VP 244 (PO 36), Per-

30 manent yellow NCG 70 (PY 16), Permanent yellow HR 70 VP 253 (PY 83) and Acetanil yellow 2GO 768 (PY 74) made by Messrs. Capelle. These pigments have a lower specific area than the pigments referred to hereinbefore and therefore a larger average particle size.

35 Very good results can also be obtained using dyes instead of pigments in colored toners. As contrasted to

5 coloring pigments, dyes are dissolved in the binder medium, usually a resin.

Examples of suitable dyes are:

Red dyes:

New Magenta (CI 42520), Chromoxane Brilliant Red
10 (CI 45180), Erosine (CI 45380), Rhodamine B (CI 45170),
Rhodamine 6 GDN (CI 45160), Rhodamine F4GDN (CI 45160),
Rhodamine B Extra (CI 45170), Rhodamine 6G (CI 45160),
Rhodamine F5GL (CI 45160), Para Rosaniline (CI 42500),
Sulpho-Rhodamine B (CI 45100), Neutral Red (CI 50040),
15 Safranine T (CI 50240).

Blue dyes:

Basic Blue 5 (CI 42140), Methylene Blue (CI 52015),
Chromoxane Brilliant Blue (CI 43850), Victoria Blue 4R
(CI 42563), Janus Blue (CI 12211).

20 Green dyes:

Astra Diamond green (CI 42040), James Green (CI 11050),
Basic Green 4 (CI 42000), Azo Green (CI 42175).

It is particularly preferred to add at least one
white pigment with high scattering power to the toner to
25 increase scattering.

Particularly good results are obtained with toners
in which the magnetic particles have the composition FeO_x
where $1.4 \leq x \leq 1.5$. The use of such an oxide as mag-
netizable component leads to brighter, saturated colors,
30 especially in yellow, green and blue toners.

The toners according to the invention are prepared
by mixing magnetizable particles, coloring agents and
binders, preferably using mixing apparatus which develop
only a low shearing force. It is advantageous to proceed
35 by adding the coloring agents and the magnetizable par-
ticles to the binder.

5 The toners according to the invention are particularly suitable for use in electrostatic photocopying systems and magnetic printers.

 The invention is described below by way of example, which is not to be regarded as implying any limitation.

10 The color assessment of the pigment mixtures is carried out after incorporation into a binder and preparation of a lacquer sample according to German Industrial Standards DIN 6174 and 55 985 since the colorimetric assessment of powders provides poorly reproducible results. The assessed characteristics of L (brightness) and C (saturation) serve unequivocally to evaluate the color of the pigment mixture, a color having a high saturation and/or brightness producing a brilliant visual impression.

20 Some coloring agents which characterize the preferred color range have been selected in the following examples. Those skilled in the art can easily select further suitable coloring agents from those agents known in the art. A commercial, easily dispersible titanium dioxide pigment with rutile structure (Bayertitan R-KB-2, Trade product of Bayer AG) is used in the examples as a suitable white pigment. Other strongly scattering white pigments (titanium dioxide anatase, zinc sulphide) may also be used.

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5 Example 1

Preparation of the platelet-shaped magnetic material

Platelet-shaped alpha-iron oxide according to Euro-
pean Patent 14 382 (=US 4,404,254) was used as starting
10 material. It has a specific surface (N_2 adsorption, BET
method) of $1 \text{ m}^2/\text{g}$. The average particle diameter is about
10 μm , the thickness of the particles, 0.05 μm .

A magnetite was prepared from the alpha-iron oxide
by reduction with moist hydrogen at 400°C for 90 minutes,
15 and the magnetite was then oxidized with air at 260°C for
180 minutes to produce the desired bronze tone. The FeO
content of the end product is 10% by weight, which
corresponds to the composition $\text{FeO}_{1.445}$. The specific
surface of the preliminary product and the particle size
20 are preserved in the end product. A scanning electron
microscopic photograph is shown in Figure 1. The magnetic
properties of the end product are characterized by a coer-
civity of 488 Oe and a magnetic saturation of 370 G
 cm^3/g .

25 Example 2

Preparation of the pigment mixture

Preparation of the mixture of platelet-shaped mag-
netic material, a coloring agent and a white pigment was
carried out by dry grinding them together in a vibration
30 grinding mill (Disintegrator of Braun/Melsungen, Teflon
grinding vessel with two agate balls) for one minute.
Other grinding or mixing apparatus could be used but care
must be taken to ensure that the platelets are not des-
troyed in the grinding process.

35 The following were used in the pigment mixtures for
the different colors:

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- 5 a. Blue
1.84 g platelet-shaped material according to Example 1
1.6 g white pigment (Bayertitan R-KB-2/Trade product of Bayer AG)
0.34 g Heliogenblau K 7080 (Trade product of BASF AG)
- 10 b. Green
1.84 g platelet-shaped material according to Example 1
1.6 g white pigment (Bayertitan R-KP-2/Trade product of Bayer AG)
0.17 g Heliogengrün 8680 (Trade product of BASF AG)
- 15 c. Yellow
0.17 g Paliotolgelb K 0961 HD (Trade product of BASF AG)
1.84 g platelet-shaped material according to Example 1
1.6 g white pigment (Bayertitan R-KB-2/Trade product of Bayer AG)
- 20 d. Red
0.17 g Paliotolgelb K 2141 HD (Trade product of BASF AG)
0.17 g Paliotolgelb K 0961 HD (Trade product of BASF AG)
1.84 g platelet-shaped material according to Example 1
0.8 g white pigment (Bayertitan R-KB-2/Trade product of Bayer AG)
- 25 0.68 g Paliogenrot 3911 K (Trade product of BASF AG).

Example 3

Preparation of the pigment mixture without grinding

- 30 To demonstrate the good dispersibility of the magnetic material of Example 1 according to the invention, a pigment mixture as in Example 2 c was prepared by simply mixing with a spatula.

Example 4

- 35 Preparation of a lacquer sample for the colorimetric assessment

1 g of the pigment mixture from Example 2 or 3 was stirred into 4 g of binder (Alkydal F 48, Trade product

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5 of Bayer AG) and mixed on a plate color trituration
machine of Engelsmann, using 2 x 100 revolutions without
a load. A lacquer sample in the form of a film 90 μ m in
thickness was produced on a white cardboard with the aid
of a stripping ruler. The lacquer film dried for 24 hours
10 before the measurement.

Example 5

Colorimetric assessment

The colorimetric assessment of the lacquer samples
according to Example 4 was carried out according to German
15 Industrial Standard DIN 6174, using a spectral color
measuring apparatus (Macbeth, Kollmorgen Corp., USA). The
measuring geometry was diffuse/8° without elimination of
gloss. For brightness H and saturation C, the values shown
in Table 1 were determined. The Table also contains the
20 data of comparison Examples A and B.

From the values given, it may be seen that the
comparison examples give substantially inferior results
in almost every case. To show this clearly, the differ-
ences in brightness values and saturation between the
25 comparison examples and the variants according to the in-
vention are given (ΔL^* , ΔC^*).

The unground sample from Example 3 even gives a
better result than the ground sample of Example 2 c. This
shows the excellent dispersibility of the magnetic, pla-
30 telet-shaped material according to the invention.

Comparison Example A

For comparison purposes, a coarse particled magnetite
was prepared from a commercial magnetic toner pigment
- Bayferrox 8610/Trade product of Bayer AG - by tempering
35

5 and reduction. Bayferrox 8610 was tempered in air for 30 minutes at 700°C and then reduced with moist hydrogen at 400°C for 120 minutes. The pigment obtained is characterized by the following data:

Coercivity:	285 Oe
10 Specific saturation	1006 Gcm ³ /g
FeO content:	31% by weight.

Pigment mixtures were prepared with this pigment in accordance with Example 2 a - d.

Comparison Example B

15 The magnetic material according to Comparison Example A was oxidized in air for 120 minutes at 280°C.

Coercivity:	178 Oe
Specific saturation:	787 Gcm ³ /g
Specific surface:	3.3 m ² /g
20 FeO content:	0.4 % by weight.

Using this pigment as magnetic component, pigment mixtures were prepared according to Example 2 a - d. A mixture was also prepared without preliminary grinding, as in Example 3 (Be).

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Table 1

Pigment mixture according to Example	Brightness L*	Saturation C*	[Comparison with reference sample]		Color Tone
			ΔL^*	ΔC^*	
A	36.2	16.0	0	0	blue
B	37.6	15.8	+1.4	-0.2	
2 a	43.4	28.0	+7.2	+12.0	
A	41.2	8.4	0	0	green
B	45.7	9.7	+4.5	+1.3	
2 b	54.3	25.9	+13.1	+17.5	
A	41.1	7.7	0	0	yellow
B	49.2	22.0	+8.1	+14.3	
2 c	59.3	32.2	+18.2	+24.5	
A	32.2	10.6	0	0	red
B	37.1	27.5	+4.9	+16.9	
2 d	39.3	27.3	+7.1	+16.7	
A	42.0	7.8	0	0	yellow
B	47.5	17.7	+5.5	+9.9	
3	67.1	36.0	+19.1	+28.2	

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What is claimed is:

1. In a colored magnetic toner containing a coloring agent and magnetizable material, the improvement wherein said magnetizable material comprises particles
10 in the shape of platelets or scale-like magnetic particles.

2. Toner according to claim 1 wherein the magnetic particles have the empirical formula FeO_x where x is 1.33
15 or more but no more than 1.5.

3. Toner according to claim 1 wherein the diameter of the platelets or scales is from 0.5 to 25 μm and their diameter/thickness ratio is at least 5.

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4. Toner according to claim 1 wherein the coloring agent has a high coloring power and contains at least one white pigment with high scattering power.

25 5. Toner according to claim 1 wherein the coloring agent is a brilliant yellow, green or blue coloring agent or a mixture thereof and the magnetic particles have the empirical formula FeO_x where x is at least 1.4 but no more than 1.5.

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6. In an improved process for the preparation of magnetic toner according to claim 1 which comprises mixing magnetizable particles, coloring agents and binders,
the improvement wherein mixing, ^{is carried out} in a mixing apparatus which produces only a low shearing force.

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7. A magnetic toner whenever made by a process according to Claim 6.

8. A magnetic toner according to Claim 1 and substantially as described in the accompanying description with particular reference to Examples 1 to 3.

5 9. In an electrostatic photocopying^{process}/wherein a copy
image is produced on copy paper with a magnetic toner, the
improvement wherein said magnetic toner is a colored
magnetic toner according to any one of claims 1 to 5, 7 and 8.

10 10. In a magnetic printing process wherein the
printed image is formed by a magnetic toner, the improve-
ment wherein said magnetic toner is a colored mag-
netic toner according to any one of claims 1 to 5, 7 and 8.

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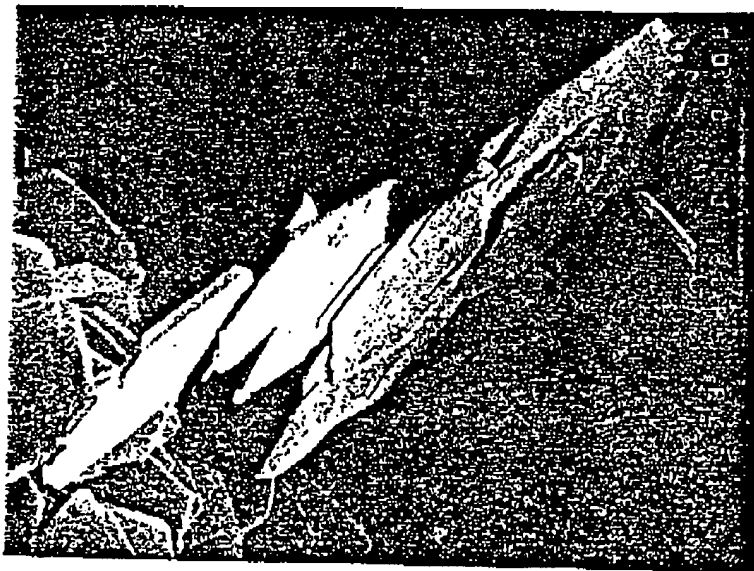


FIG. 1

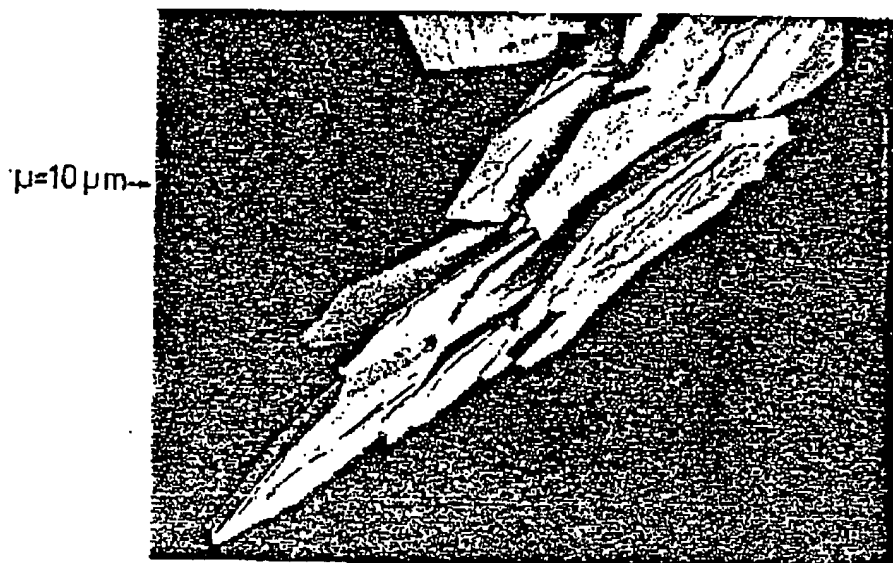


FIG. 2

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